

**METHOD FOR PREPARATION OF HEAT-HARDENING FLEXIBLE FOAM  
SUBSTANCES THAT HAVE URETHANE GROUPS AND REDUCED COMPRESSIVE  
STRENGTHS**

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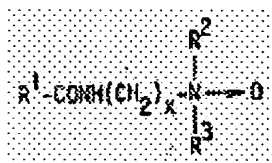
METHOD FOR PREPARATION OF HEAT-HARDENING FLEXIBLE FOAM  
SUBSTANCES THAT HAVE URETHANE GROUPS AND REDUCED COMPRESSIVE  
STRENGTHS

[Verfahren zur Herstellung von heisshärtenden, flexiblen, Urethangruppen aufweisenden  
Schaumstoffen mit verminderter Stauchhärte]

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The invention concerns a method for preparation of heat-hardening flexible foam substances that have urethane groups and reduced compressive strength, by the reaction of polyethers that are of a molecular weight from 400 to 12000 and that have at least two hydroxyl groups with polyisocyanates in the presence of catalysts and water and optionally in the presence of emulsifiers, stabilizers, cross-linking agents, blowing agents and conventional auxiliary agents and additives. The method is characterized by the fact that it is carried out in the presence of 0.01 to 3 parts by weight, with respect to 100 parts by weight polyol, of amine oxides of the general formula



where

$R^1$  is an alkyl residue or a mixture of alkyl residues with 7 to 17 carbon atoms,

$R^2$  and  $R^3$  are alkyl residues with 1 to 4 carbon atoms, and

$x$  is 2 or 3.

The method for producing heat hardening polyurethane soft foams with reduced compressive strength in accordance with the invention does not require any physical blowing agents like fluorochlorocarbons, methylene chloride, pentane, acetone and 1,1,1-trichloroethane or requires amounts that are considerably reduced in comparison with the conventional methods of the prior art.

Particularly, foams are prepared by the method in accordance with the invention by introducing the foamable reaction mixture into a closed mold.

Nonrigid polyurethane foams are widely used in the upholstered furniture and automobile industries. For the various uses and the various qualities that derive from these uses it is necessary to be able to vary the compressive strength over a wide range, in addition to being able to vary the raw density.

Inert inorganic or organic fillers are already being used to produce foams with increased compressive strength. The compressive strength can also be increased by using the so-called filler-containing polyols, which are produced by polymerization reactions of unsaturated monomers or addition reactions in the polyols that serve for foaming.

A reduction of the compressive strength is achieved by the co-use of physical blowing agents such as fluorochlorocarbons or methylene chloride. This is contrary to the effort to reduce the use of fluorochlorocarbons as much as possible, for environmental reasons. This also applies to methylene chloride, which is physiologically not safe.

\* [Numbers in the margin indicate pagination of the foreign text.]

This also is applicable to a certain extent to other physical blowing agents, the emission of which is highly restricted, for instance in the Federal Republic of Germany by the industrial guidelines for air, and in many other countries in a similar way.

The raw density of flexible polyurethane soft foams generally lies in the range between 14 and 50 kg/m<sup>3</sup>. Typical values of the compressive strength at 40% compression are 1.0 to 6.0 kPa. If the amount of physical blowing agent used in foaming is reduced, then foams with comparably higher density and compressive strength will again result. This increase of the density can be counteracted by increasing the amount of added water, but the compressive strength in this case will still remain at the undesirable high level.

This invention is based on the technical problem of finding a method that allows flexible polyurethane foams with lower compressive strength – for the resulting volumetric weight – to be prepared while reducing the amount of physical blowing agents, in particular fluorochlorocarbons or methylene chloride, and with a possibly tolerable increase of the amount of added water.

It is known from EP-A-0 358 282 that in a method of the kind mentioned at the start the amount of fluorocarbons that is to be used can be reduced if foaming is carried out in the presence of 0.001 to 1 part by weight, with respect to 100 parts by weight polyol, of one or more uncross-linked, water-soluble polyelectrolyte with a molecular weight from 1000 to 20,000,000. Alkali salts of polyacrylates having a molecular weight from 2000 to 10,000, in amounts from 0.01 to 0.5 parts by weight per 100 parts by weight polyol, are preferably to be used. /3

DE Patent 40 29 081 describes a similar method in which defoaming is carried out in the presence of 0.01 to 1.0 parts by weight, preferably 0.05 to 0.8 parts by weight, with respect to 100 parts by weight polyol, of one or more alkali salts of particular hydroxycarboxylic acids.

It is common to all of the products that in the continuous production of polyurethane foams by the method foam slabstock production they allow the production of heat-hardening soft foams with clearly reduced compressive strength, without problems coming up in the technical processing regard. A negative, unacceptable influence on the part of the other physical parameters of the foam absolutely does not take place.

However, the described products are less well suited for the preparation of heat-hardening polyurethane soft foams by the foam molding method. In spite of a likewise clear reduction of the compressive strength, the molded foams that are produced have a strong tendency to be close-celled, and as a consequence tend to shrink. The so-called processing tolerance accordingly is greatly limited through the use of such softening additives which cannot be counteracted even by an adjustment in catalysis, which is the usual step in such cases.

Moreover, the molded foams have an unacceptable, highly increased compression set. The compression set enables predictions to be made about the long term behavior of foams in

practice under continuous and variable loading. Values that are as low as possible are desired since they allow one to expect permanently high user properties for the foams.

This invention is based on the solution of the technical problem of finding a method for producing heat hardening flexible polyurethane soft foams in which

a) the use of physical blowing agents in general, but especially fluorochlorocarbons and even methylene chloride, can be avoided or at least considerably limited,

b) the resulting foams have the desired low volumetric weight with reduced compressive strength,

c) production both by the continuous slabstock method and the foam molding method is possible, without processing problems arising due to the method and without an adverse effect on the compression set taking place.

Preferably 0.01 to 1.5 parts by weight amine oxide is used in the method in accordance with the invention.

Residue  $R^1$  preferably derives from naturally occurring fatty acids at the general formula  $R^1COOH$  or their mixtures. Fatty acids of the type of coconut fatty acid are especially preferred, where optionally the lower fatty acids with fewer than 10 carbon atoms are removed from the mixture of fatty acids by distillation. However, pure fatty acids such as lauric, palmitic, myristic or steric acid, can also be used to produce the amine oxide.

The residues  $R^2$  and  $R^3$  are preferably straight-chain alkyl residues with 1 to 4 carbon atoms, with methyl residues being preferred.

x preferably has a value of 3.

The amine oxides that are to be used in accordance with the invention can be prepared in the way known to the specialist by oxidation of fatty acid amide dialkylamines with aqueous  $H_2O_2$  solutions.

To conduct the method in accordance with the invention, it is expedient to prepare a concentrated aqueous solution of the amine oxides that are to be used in accordance with the invention. Then in conducting the process this solution is added separately or to the so-called activator solution, which consists of water, stabilizer and amine catalysts, or to the polyol or to a partial amount of a polyol or to a partial amount of a polyol. Through this the amount of water introduced into the system is low and moreover can take into account the amount of water needed for the foaming.

The processing tolerance within the formulation is sufficiently large to guarantee a reproducible procedure with reproducible product properties.

Through the addition of the amine oxide to be used in accordance with the invention in the given concentration range the other foam properties apart from the compression hardness, especially the compression set, are not adversely affected in a crucial way.

Otherwise, the method for producing polyurethane soft foams can be carried out in the usual way and with the starting substances known from the prior art.

The following are used as polyisocyanates for the production of the polyurethane soft foams: aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic isocyanates, as are described, for example by W. Seifken in Justus Liebigs Annalen der Chemie, 562, pp. 75 to 138, for example one of the general formula



in which

n is 2 to 4, preferably 2, and

Q is an aliphatic hydrocarbon residue with 2 to 18, preferably 6 to 10 carbon atoms, a cycloaliphatic hydrocarbon residue with 6 to 15, preferably 5 to 10 carbon atoms, and aromatic hydrocarbon residue with 6 to 15, preferably 6 to 13 carbon atoms, or an araliphatic hydrocarbon residue with 8 to 15, preferably 8 to 13 carbon atoms.

Examples of suitable polyisocyanates are described in DE-OS

The following are preferably used as polyisocyanates in the method in accordance with the invention: polyisocyanates of the type of diphenylmethane diisocyanate and/or toluene diisocyanate, for example 2,4- and 2,6-toluene diisocyanate, as well as any mixtures of these isomers (TDI), 4,4' and/or 2,4'-diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate and/or isophorone diisocyanate, polyphenylpolymethylene polyisocyanate, as are prepared by aniline-formaldehyde condensation followed by phosgenation ("raw MDI"), also polyisocyanates that derive from 2,4- and/or 2,6-toluene diisocyanate or from 4,4'- and/or 2,4'-diphenylmethane diisocyanate that have been modified by carbodimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups and biuret groups, also alkyl-substitute NDI types as are described, for example, in DE-OS 29 35 318 and DE-OS 30 32 128.

Especially preferred are:

toluene diisocyanate as a mixture of the 2,4- and 2,6-isomers in an 80:20 ratio (TDI 80),  
toluene diisocyanate as a mixture of the 2,4- and 2,6-isomers in a 65:35 ratio (TDI 65),  
toluene diisocyanate prepolymers,

mixtures of TDI with diphenylmethane diisocyanate and/or polyphenylpolymethylene polyisocyanates.

The polyethers having at least two hydroxyl groups that are suitable have a molecular weight from 400 to 12,000 and a functionality of preferably 2 to 8, where polyether polyols with terminal hydroxyl groups are preferred. The polyols are in general prepared by adding ethylene oxide and/or propylene oxide to low-molecular, polyhydric alcohols like glycerol or trimethylolpropane.

Other polyols are known to the specialist and can be taken, for example, from EP-A-0 380 993.

In general amines like triethylenediamine, bis(2-dimethylaminoethyl)ether, N,N-dimethylethanolamine, N,N,N',N'', N''-pentamethyldiethylenetriamine, N-methylmorpholine, dimethylbenzoamine, tertiary alkylphosphene, tin(II) octoate, dibutyltin(IV) laurate and chelates of metals, for example chelates of the acetyl acetate of magnesium, zirconium or nickel, can be used as catalysts. The catalyst is used in amounts from 0.01 to 1.0 parts by weight, with respect to 100 parts by weight polyol.

Other conventional additives are flame retardants, fillers, pigments, plasticizers, antistatic agents and cell regulation agents. These and other auxiliary agents are known to the specialist.

If the preparation of polyurethane soft foams by the method of the prior art and the method in accordance with the invention using various formulations is shown in the following examples.

The following products and product names are used in the examples:

Polyol A: commercial polyether triol for the production of flexible polyurethane foams by the continuous slab method with exclusively secary OH end groups and an ethylene content of about 11%, OH number 48, MW = 3500 g/mol.

Polyol B: commercial polyether triol for the production of flexible polyurethane foams by the continuous slabstock method with exclusively secary OH end groups based on propylene oxide, OH number  $\approx$  56, MW = 3000 g/mol.

Polyol C: commercial polyether triol for the production of polyurethane foams by the foam molding method with about 50 to 60% primary OH end groups and an ethylene oxide content of about 12 to 14%, OH number = 42, MW = 4000 g/mol.

TEGOSTAB® BF 2370: commercial foam stabilizer sold by Th. Goldschmidt AG, Essen.

TEGOSTAB® B 4000: commercial foam stabilizer sold by Th. Goldschmidt AG, Essen. /5

Niax® A 107: commercial amine catalyst sold by Union Carbide Corporation, USA.

TEGOAMINE® PTA: commercial amine catalyst sold by Th. Goldschmidt AG, Essen. used in accordance with the invention

Compound A: 1-alkylamino-3-dimethylaminopropane-3 N-oxide as 35% solution in water, where alkyl means a mixture of C<sub>7</sub> through C<sub>17</sub>.

Comparison substance I: corresponding to EP-A-0 358 282, commercially available under the trade name Carapor® 2001 from Shell AG, Eschborn (Taunus).

Comparison substance II: corresponding to DE Patent 40 29 081, commercially available under the trade name ORTEGOL® 310 from Th. Goldschmidt AG, Essen.

The foams are prepared by the so-called method of hand foaming. Here all of the components up to the polyisocyanate and optionally the physical blowing agent are stirred for 60 sec at 1000 rpm. Then the polyisocyanate and optionally the blowing agent are added and stirring is carried for another 7 sec at 2500 rpm.

According to the method of slabstock foaming the liquid mixture is then poured into a container measuring 30 x 30 x 30 cm that is open at the top, so that the foam can freely rise.

Foam pieces are prepared by the slabstock foaming method by introducing the reactive mixture into a metal mold measuring 40 x 40 x 12 cm that can be sealed on all sides and that has been heated to 60°C. Then it is heated to 120°C in a period of 10 min and then the foam is unmolded.

The determination of the foam properties takes place after 72 h of storage under normal conditions, i.e.,  $23 \pm 1^\circ\text{C}$  and  $50 \pm 2\%$  relative air humidity. The following properties are determined:

The volumetric weight is determined by exact weighing and measurement of a foam piece about 10 x 10 x 10 cm in size and is expressed in  $\text{kg/m}^3$ .

The compressive strength is determined by DIN 53 577 at 40% compression.

Determination of air permeability (open cell quality). The air permeability is understood to mean the back pressure in a column of water that arises when a uniform stream of air at 8 L/min is passed through the foam object. Lower values (less than 50) mean good air permeability and thereby a good open cell quality. High values (greater than 100), in contrast, correspond to a higher fraction of closed cells. As high a degree of open cell quality as possible is desired.

The compression set after constant deformation ("DVR") is the ratio of the difference of the height of the sample before and after application of pressure and of the original height of the sample, in the teaching of DIN 53 572.

The following conditions for compression, temperature and duration of load were used to conduct the tests:

DVR (dry)     50%, 70°C, 22 h

DVR (wet)     50%, 50°C, 22 h, 100% relative air humidity

#### Examples 1 to 5 and Comparative Examples I through VI

The mode of action of the amine oxides to be used in accordance with the invention for the production of flexible polyurethane foams with reduced compressive strength by the continuous slabstock method is illustrated in Examples 1 to 5 and the results are compared with compounds of the prior art, see Comparative Examples I through VI in Table 1.



If 4.0 parts by weight water are used one obtains a foam with a volumetric weight of  $24 \text{ kg/m}^3$  and compressive strength of 3.0 kPa (Comparative Examples I and II). The same volumetric weight is achieved if one used 3.3 parts by weight water in combination with 7 parts by weight trichlorofluoromethane, but this foam is considerably softer (compressive strength 2.0 kPa, Comparative Example III). The situation is similar for the use of methylene chloride (Comparative Example IV). In order to obtain both the volumetric weight and the low compressive strength without the co-use of physical agents, the higher water content of Example 1 and the use of the compounds in accordance with the invention are necessary (Examples 1 to 5).

Thus about 7 parts by weight physical blowing agent can be replaced by the combination of a higher water content and the plasticizing additive.

Example 5 shows that this is independent of the type of polyol.

Comparison with Comparative Examples V and VI confirms that the plasticizing effect of the amine oxides used in accordance with the invention is just as highly expressed as in the case of the comparison substances I and II in correspondence with the prior art.

One can further see from the table that in all of the examples foams with comparably good compressive set (dry and wet) with simultaneously good open cell quality are formed.

Thus there is no effect on the working tolerance (Examples 1 to 5).

Table 1. Formulation (slabstock foam, data in wt%)

Beispiel bzw. Vergleichsversuch	I	II	III	IV	I	2	3	4	5	V	VI
Polyol A	100	-	100	-	100	100	100	100	-	100	100
Polyol B	-	100	-	100	-	-	-	-	100	-	-
Wasser (gesamt)	4,0	4,0	3,3	3,2	4,0	4,0	4,0	4,0	4,0	4,0	4,0
TEGOSTAB <sup>®</sup> BF 2370	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0
TEGOANIN <sup>®</sup> PTA	0,15	0,17	0,22	0,22	0,15	0,15	0,15	0,15	0,17	0,15	0,15
Zinn(II)-octoat	0,20	0,20	0,20	0,20	0,20	0,20	0,20	0,20	0,20	0,20	0,20
Verbindung A	-	-	-	-	0,4	1,0	2,0	3,0	3,0	-	-
Vergleichs- substanz I	-	-	-	-	-	-	-	-	-	0,6	-
Vergleichs- substanz II	-	-	-	-	-	-	-	-	-	-	1,0
Trichlorfluor- methan	-	-	7	-	-	-	-	-	-	-	-
CH <sub>2</sub> Cl <sub>2</sub>	-	-	-	8	-	-	-	-	-	-	-
TDI 80	48,3	49,7	41,2	41,6	48,3	48,3	48,3	48,3	49,7	48,3	48,3
Raumgewicht (kg/m <sup>3</sup> )	24,0	24,1	23,9	23,7	24,0	24,1	24,1	24,0	24,2	24,0	24,1
Stauchhärte (kPa)	3,0	3,0	2,0	1,8	2,6	2,5	2,3	2,1	2,0	2,0	2,0
Offenzellig- keit	17	26	33	20	16	14	9	8	10	7	18
DVR (trocken)	2	2	2	2	2	2	3	3	2	3	2
DVR (feucht)	4	4	3	3	3	4	4	5	4	4	5

- Key:
- 1 Example or Comparative Example
  - 2 Water (total)
  - 3 Tin(II) octoate
  - Compound A
  - Comparison substance I
  - Comparison substance II
  - Trichlorofluoromethane
  - 4 Volumetric weight (kg/m<sup>3</sup>)
  - Compressive (kPa)
  - Open cell quality
  - DVR (dry)
  - DVR (wet)

#### Examples 6 and 7 and Comparative Examples VII through XIX

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Examples 6 and 7 and Comparison Examples VII and VIII as well as XIII through XV show that when compound A is used five, or nine, parts of trifluorochloromethane can be replaced, in each case according to the water content of the formulation. There is just as little adverse effect on the compression set both in wet and dry state in the given concentration range

as on the open cell quality. In all cases shrinkage-free molded articles are obtained. The results can be seen from Table 2.

A softening effect with, however, highly increased compression set and a tendency to shrink because of the increased closed cell quality can also be seen when using comparison substances I and II (Comparative Examples IX through XII and XVI through XIX). The advantages of the amine oxides used in accordance with the invention therefore are obvious.

Table 2. Formulations (molded foam, date in wt%)

Beispiel bzw. Vergleichsversuch (1)	VII	6	VII/1	IX	X	XI	XII	XIII
Polyol C	100	100	100	100	100	100	100	100
Wasser (gesamt) (2)	4,0	4,0	3,5	4,0	4,0	4,0	4,0	5,5
TEGOSTAB® B 4900	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0
N-Methylmorpholin (3)	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,4
Niex® A 107	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,4
N,N-Dimethylcetylamin	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,4
Zinn(II)-octoat	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,15
Verbindung A	-	1,0	-	-	-	-	-	-
Vergleichssubstanz I	-	-	-	0,3	0,6	-	-	-
Vergleichssubstanz II	-	-	-	-	-	0,2	0,6	-
Trichlorfluormethan	-	-	5	-	-	-	-	-
TDI 80	45,2	45,2	40,3	45,2	45,2	45,2	45,2	59,7
Raumgewicht (kg/m³)	26,0	26,9	26,6	26,8	26,7	26,9	26,6	18,8
Stauchhärte (kPa)	3,0	2,5	2,5	2,7	nicht (6)	2,6	nicht (6)	2,9
DVR (trocken)	4	4	7	15	bestimmbar	13	bestimmbar	8
DVR (feucht)	7	6	13	40	bestimmbar	42	bestimmbar	19
Offenzelligkeit	200	80	280	> 300 (8)	>> 300 (9)	> 300 (8)	>> 300 (9)	150
Schumpverhalten	1,0 (7)	1,0 (7)	1,0 (7)	schwach	sehr stark	schwach	sehr stark	1,0 (7)

Beispiel bzw. Vergleichsversuch (1)	7	XIV	XV	XVI	XVII	XVII/1	XIX
Polyol C	100	100	100	100	100	100	100
Wasser (gesamt) (2)	5,5	4,6	4,5	5,5	5,5	5,5	5,5
TEGOSTAB® B 4900	2,0	2,0	2,0	2,0	2,0	2,0	2,0
N-Methylmorpholin (3)	0,4	0,4	0,4	0,4	0,4	0,4	0,4
Niex® A 107	0,4	0,4	0,4	0,4	0,4	0,4	0,4
N,N-Dimethylcetylamin	0,4	0,4	0,4	0,4	0,4	0,4	0,4
Zinn(II)-octoat	0,15	0,15	0,15	0,15	0,15	0,15	0,15
Verbindung A	2,5	-	-	-	-	-	-
Vergleichssubstanz I	-	-	-	0,4	0,6	-	-
Vergleichssubstanz II	-	-	-	-	-	0,2	0,6
Trichlorfluormethan	-	7	9	-	-	-	-
TDI 80	59,7	52,9	50,9	59,7	59,7	59,7	59,7
Raumgewicht (kg/m³)	18,8	18,2	18,5	18,7	18,4	18,6	18,8
Stauchhärte (kPa)	2,0	2,2	2,0	2,3	nicht (6)	2,4	nicht (6)
DVR (trocken)	6	11	13	19	bestimmbar	17	bestimmbar
DVR (feucht)	16	15	20	45	bestimmbar	46	bestimmbar
Offenzelligkeit	13	130	250	> 300 (10)	>> 300 (9)	> 300 (10)	>> 300 (9)
Schumpverhalten	1,0 (7)	1,0 (7)	1,0 (7)	mittel	sehr stark	mittel	sehr stark

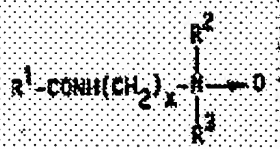
i.O. = normal, no shrinkage

Key:	1	Example or Comparative Example
	2	Water (total)
	3	N-methylmorpholine
	4	N,N-dimethylcetylamine
		Tin(II) octoate
		Compound A
		Comparison substance I
		Comparison substance II
		Trichlorofluoromethane
	5	Volumetric weight (kg/m <sup>3</sup> )
		Compressive strength (kPa)
		DVR (dry)
		DVR (wet)
		Open cell quality
		Shrinkage behavior
	6	Not determinable
	7	I.O.
	8	Weak
	9	Very strong
	10	Average

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#### Claims

1. Process for the preparation of thermocuring, flexible, urethane group-containing foams of reduced compressive strength by reacting polyethers containing at least two hydroxyl groups and having a molecular weight of from 400 to 12,000 with polyisocyanates in the presence of catalysts and water and optionally in the presence of emulsifiers, stabilizers, crosslinking agents, blowing agents and conventional auxiliaries and additives, characterized in that the process is carried out in the presence of from 0.01 to 3 parts by weight, based on 100 parts by weight of polyol, of amine oxides of the general formula



where

- R<sup>1</sup> is an alkyl radical or a mixture of alkyl radicals having 7 to 17 carbon atoms,  
 R<sup>2</sup> and R<sup>3</sup> are alkyl radicals having 1 to 4 carbon atoms, and  
 x is 2 or 3.

2. Process according to Claim 1, characterized in that from 0.01 to 1.5 parts by weight of amine oxide are used.
3. Process according to Claim 1 or 2, characterized in that an amine oxide is used in which R<sup>1</sup> is a mixture of alkyl radicals having 7 to 17 carbon atoms derived from the fatty acid mixture of coconut fatty acid, R<sup>2</sup> and R<sup>3</sup> are methyl radicals, and x has a value of 2.
4. Process according to Claim 1 or 2, characterized in that the amine oxide or the concentrated aqueous solution thereof is added separately to the foaming batch or is added to the activator solution comprising water, stabilizer and amine catalyst, or to the polyol or a part-amount of a polyol.

European  
Patent Office

Application Number  
EP 92 11 4357

### EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>5</sup> )
A	US-A-3 173 896 (R.K. ADAMS ETA AL.) * Claims 1-3 * * Column 4, Line 29 – Line 39 * * Column 4, Line 70 – Column 6, Line 72 * ---	1	C08J9/00 C08K5/32 C08K5/20 //C08L75:04
A	US-A-3 173 173 897 (R.K. ADAMS ETA AL.) * Claims 1-3,5,6 * * Column 4, Line 45– Line 66 * -----	1	<div>TECHNICAL FIELDS SEARCHED (Int. Cl.<sup>5</sup>)</div> <div>C08J C08K C08G</div>
The present search report has been drawn up for all claims.			
Place of search The Hague		Date of completion of the search January 6, 1993	Examiner M.A. Van Puymbroeck
<b>CATEGORY OF CITED DOCUMENTS</b>  <div> X: Particularly relevant if taken alone.  Y: Particularly relevant if combined with another document of the same category.  A: Technological background.  O: Non-written disclosure.  P: Intermediate document. </div> <div> T: Theory or principle underlying the invention.  E: Earlier patent document, but published on, or after the filing date.  D: Document cited in the application.  L: Document cited for other reasons.  .....  &amp;: Member of the same patent family, corresponding document. </div>			